STUDIES ON THE CONSTITUTION OF QUEBRACHO TANNIN

BY

FREDERICK GROSSER

B.S., Wheaton College, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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Introduction

Quebracho tannin is a commercial tanning material extracted from the bark or wood of the quebracho tree. Quebracho, which is a contraction of the Spanish *quebra-hacho* meaning "axe-breaker" is a name applied to several varieties of trees of Central and South America whose wood is extremely hard. Commercial quebracho extract for tanning purposes, however, is obtained from two closely related species of tree of the order *Anacardiaceae,* namely *Quebrachia Lorentzii,* Gris. and *Schinopsis Balansae,* Engl., both of which are known under the more common name quebracho colorado.

The exact chemical nature of the constituents of quebracho tannin is not known. Various investigators have suggested different possible structures. Evidence seems to indicate that the material consists of a mixture of closely related compounds. Recently, from consideration of the degradation products from quebracho extract, namely hydroquinone, resorcinol, phloroglucinol and catechol, Nunez[1] proposed two possible structures, 3,4,6,3′,4′-pentahydroxy-2-benzylcoumaran and 3,4,7,3′,4′-pentahydroxy-2-benzylcoumaran.

The purpose of this work was to synthesize 3,4,6,3′,4′-pentahydroxy-2-benzylcoumaran and compare it with the carefully purified material obtained from quebracho extract, in an effort to prove or disprove its presence in the natural product. Because of the sensitivity of polyhydroxy compounds of this type to oxidation, it was thought that the acetylated or benzoylated derivatives might be more suitable compounds for comparison.

Theoretical and Experimental

Several methods are available for the preparation of coumaranones substituted in the two position. The method

for preparing the desired 3,4,6,3′,4′-pentahydroxy-2-benzylcoumaran which seemed most likely to succeed involved preparation of 4,6-dihydroxycoumaran-3-one according to the method of Sonn[2] and Auwers[3], condensation of this coumaranone with protocatechuic aldehyde[4], and catalytic reduction[5] of the resultant 4,6,3′,4′-tetrahydroxy-2-benzalcoumaran-3-one to 4,6,3′,4′-tetrahydroxy-2-benzylcoumaran-3-one. The last reaction might proceed directly to the desired 3,4,6,3′,4′-pentahydroxy-2-benzylcoumaran if it were catalyzed with hydrochloric acid[6].

Difficulty was encountered in the condensation reaction which, under a variety of conditions, invariably yielded amorphous, highly colored products which did not have a common decomposition point. Use of the corresponding acetylated derivatives in the condensation reaction failed to produce a crystalline product. However, with the corresponding benzoylated compounds, the condensation reaction proceeded satisfactorily. The catalytic reduction of 4,6,3′,4′-tetrabenzoyloxy-2-benzalcoumaran-3-one produced 4,6,3′,4′-tetrabenzoyloxy-2-benzylcoumaran-3-ol directly, even when uncatalyzed by hydrochloric acid. Saponification produced the desired 3,4,6,3′,4′-pentahydroxy-2-benzylcoumaran. The pentaacetate was also prepared.

Quebracho tannin is classed with the phlobatannins[7]. Tannins of this type are converted to dark red or brown, amorphous, insoluble compounds known as phlobaphenes when they are heated with dilute hydrochloric acid.

To obtain quebracho tannin for comparison with the synthetic compound, quebracho powder was extracted with water. The tannin was salted out of its aqueous solution with sodium chloride. The precipitate was extracted with acetone, and the residue obtained on evaporation of the acetone solution was washed with ether. The tannin was further purified by precipitation from its solution in absolute alcohol with anhydrous ether.

The tannin was also obtained by extracting quebracho powder with alcohol. Phlobaphenes were precipitated by the

addition of water to the alcoholic solution, and removed by filtration. The tannin was precipitated from its alcoholic solution as the lead salt. Decomposition of the lead salt with hydrogen sulfide yielded lead sulfide, which was removed by filtration. The tannin was obtained by evaporation of the alcoholic filtrate, and purified by precipitation from a solution in absolute alcohol with anhydrous ether.

The tannin obtained varied in color from pink to red, was amorphous, and decomposed at temperatures ranging from 250-350° on the Maquenne block. When dry, it appeared to be stable, but when moist it rapidly formed a tar on exposure to the atmosphere. The acetylated and benzoylated derivatives of the tannin, prepared by various methods, were also amorphous compounds which decomposed at relatively high temperatures, 190-270°.

Inasmuch as 3,4,6,3′,4′-pentahydroxy-2-benzylcoumaran and its acetate are crystalline compounds which melt at 259-262° and 173-174° respectively, it is evident that quebracho tannin possesses some other structure.

Summary

3,4,6,3′,4′-Pentahydroxy-2-benzylcoumaran was synthesized by the following sequence of reactions. Phloroglucinol plus chloroacetonitrile → 2,4,6-trihydroxyphenyl ∝-chloromethylketimide hydrochloride→2,4,6-trihydroxy-∝-chloroacetophenone→4,6-dihydroxycoumaran-3-one→4,6-dibenzoyloxycoumaran-3-one. 3,4-Dibenzoyloxybenzaldehyde plus 4,6-dibenzoyloxycoumaran-3-one→4,6,3′,4′-tetrabenzoyloxy-2-benzalcoumaran-3-one → 4,6,3′,4′-tetrabenzoyloxy-2-benzylcoumaran-3-ol → 3,4,6,3′,4′-pentahydroxy-2-benzylcoumaran. 3,4,6,3′,4′-Pentaacetoxy-2-benzylcoumaran was also prepared.

Quebracho tannin was obtained from quebracho powder by three different methods, and its acetylated and benzoylated derivatives were prepared. The tannin was a pink to red, amorphous material, sensitive to heat, light and oxidation, and decomposed at temperatures ranging from 250-350°. The ace-

tates and benzoates were also amorphous compounds which decomposed at relatively high temperatures. The amorphous derivatives obtained from quebracho extract were quite different from the synthetic compounds.

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VITA

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